

Antimonytrioxide extraction from stibnum ore by hydrometallurgical method[†]

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§ The importance and origin of the problem

Because Thailand has a large quantity of stibnum ores. But these are mostly of low grade, which makes it unsuitable to extract them by using heat (pyrometallurgy). The study of chemical methods of extraction will be beneficial because, apart from being economical, they better facilitate the control of the various variables involved. Also nowadays there is a continuous increase in the amount of Sb_2O_3 in industry. Preparation of Sb_2O_3 from stibnum metal has quite a high cost. Therefore there need to be a research towards methods of preparing Sb_2O_3 directly from the stibnum ore which will help reduce greatly both the number of processing steps as well as the cost of production.

§ Purpose

The purpose of this experimental work is in order to find a suitable condition for the preparation of Antimonytrioxide directly from stibnum ores with the use of a hydrometallurgical process, by investigating the influence of those variables which affect the solubility, namely the temperature and time of leaching, the concentration of the leaching reagent used, and the concentration of the solution.

§ Abstract

Antimonytrioxide (Sb_2O_3) can be directly and efficiently prepared from antimony ores by the hydrometallurgical process one method of which is acid leaching. By studying the influence of the various variables which effect the efficiency of leaching, the sizes, and the shapes of Sb_2O_3 crystals, it has been found that a suitable condition for the preparation of Antimonytrioxide from a stibnum ore which contains approximately 35.3% of Sb is by leaching it in the hydrochloric

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acid solution of ferric chloride at the temperature around 70–90°C requires approximately 1–1.5 hours by using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ approximately 10–20% in excess.

§ 1. Introduction

Antimonytrioxide (Sb_2O_3) is one of the major compounds of antimony. It is in the form of white crystals, has two types of structure, namely cubic (Senamonite) and rhombic (Valentinite), the molecular weight 291.5, the melting point 656°C, the boiling point 1,425°C, the specific gravity 5.2, and the hardness 2.0–2.5 Mohs scale. The solubility in water is 0.01 g/l at 100°C, slightly soluble in basic solution with increasing solubility as the basicity and the temperature of the solvent increase, highly soluble in the hydrochloric and the sulphuric acid, insoluble in the nitric acid, highly soluble in sulfide where the result is the thioantimonate solution, and extremely high solubility in the tartaric acid where it results in the antimony tartate solution.

§ Usage of antimony trioxide

1. Used as opacifier and emulsifier in enamel production. Being at the same time a good opacifier and a good emulsifier, Sb_2O_3 makes quality enamel that gives an enduring and glossy surface.
2. Used as pigment and lacquer. Sb_2O_3 makes good white pigment which has low rate of oil absorption (approximately 11–13 g / 100 g pigment), can withstand chemicals, light and heat.

Because Sb_2O_3 has a crystalline structure, it helps make strong pigment films. But paints which have Sb_2O_3 as pigment will dry slowly and soft, therefore it is often used together with ZnO in order to make pigments which dry quicker, stronger and have high adhesive strength.

Furthermore, Sb_2O_3 is a fireproof material that is waterproof, rust-proof and insulate against heat, which makes it popular in making paints for ships, buildings and cables.

3. Used in glass and ceramic industries. Sb_2O_3 is used as decolouriser and clarifier in the manufacturing of glass. The green colour of FeO in glass normally affects its colour, glossiness and transparency. But if Sb_2O_3 is added while the glass is melted, it will sink down in the middle, and upon being heated will act as a decolouriser by reacting with FeO. Apart from this, at a very high temperature Sb_2O_3 will undergo a reduction reaction by releasing

O₂. At the same time, it can be volatile at high temperature. The release of O₂ and volatile gas by Sb₂O₃ helps eliminating air bubbles produced while the glass melts, and gives a more transparent glass, that is it acts as a clarifier.

4. Used as flame retardants in fibres and plastics. Flame retardants in general have the following properties.

- 4.1 Reduce the combustion of fibres,

- 4.2 prevent the spreading of flame,

- 4.3 reduce the effect of heat on combustion,

- 4.4 prevent smoke creation.

An ideal flame retardant when heated should produce a substance which can destroy the combustion mechanism. This function is called *synergetic system*. For example, Sb₂O₃ in halogen polymer after heating fibres which are treated with Sb₂O₃ there will be chloride smoke produced which will reduce the air for the flame and finally extinguish it.

Sb₂O₃

in certain kinds of plastic not only helps reduce the ability to burn, but also help increase the resistance to heat, light and air.

Also, in the United States Sb₂O₃ has been widely used as flame retardants in wall papers and kitchen utensils. But in the case of flame retardant in carpets, hydrated aluminium oxide has more advantages because Sb₂O₃ when used in combination with some of the fillers in carpets will release toxic gases.

5. Other usages.

- 5.1 Used in combination with antimony sulphide as filler in rubber industry,

- 5.2 used as precipitant in manufacturing titanium white,

- 5.3 added in petrol to reduce pollution,

5.4 used as catalysts in synthetic processes,

5.5 *etc.*

From the statistics of usage of antimony compounds in industry we find that antimony trioxide is the most useful, which is used mainly as flame retardant. We find that during the past 5 to 10 years the amount of Sb_2O_3 used as flame retardant in various kinds of material in Japan and the United States has rapidly increased, as can be seen in the table which forecast the amount of Sb_2O_3 compounds used in 2000 for the US.

Usage	1984	1985	1986	1987	1988
flame retardants	8,181	7,409	7,961	8,122	8,796
glass	311	298	183	199	294
paint/pigment	275	137	107	97	73
export (estimate)	21	24	24	32	75
others	410	279	212	126	130
total	9,198	8,147	8,687	8,576	9,368

Table 1 Usage of Sb_2O_3 in Japan (tonnes). **source:** statistics of Nissho Iwai Co. Japan.

Country	1984	1985	1986	1987	1988
S. Korea	–	–	10	69	44
China	1,076	1,103	1,950	2,194	4,066
Taiwan	–	36	36	51	139
Hong Kong	17	34	35	–	24
France	99	112	252	300	258
Belgium	2	–	18	24	54
Italy	–	–	–	–	–
U.K.	1,000	1,212	1,117	1,578	1,359
USSR	241	160	80	87	24
USA	2	15	91	35	108
Mexico	30	–	20	28	72
Bolivia	–	–	–	–	–
S. Africa	–	–	–	2	–
total	2,467	2,672	3,609	4,368	6,188

Table 2 Antimony trioxide import in Japan (tonnes). **source:** statistics of Nissho Iwai Co. Japan.

End use	1983	statistical projections	2000 contingency forecasts for USA		
			Forecast range		probable
			Low	High	
transportation	11,500	23,000	5,000	26,000	13,000
flame retardants	10,000	23,700	10,000	25,000	20,000
rubber products	1,000	3,900	500	1,500	1,000
chemicals	2,000	7,600	2,500	5,000	3,000
ceramics and glass	1,800	2,800	1,500	3,000	2,500
machinery	1,800	1,000	1,000	2,500	1,500
other	1,612	0	1,500	3,000	2,000
total	29,712	–	22,000	66,000	43,000

Table 3 Predicted usage of antimony trioxide in 2000 of the United States (tonnes). **source:** statistical projections, provided by the branch of Economic Analysis are derived from regression analyses based on 24 year historical time series data and from forecasts of economic indicators such as GNP and FRB index. A statistical projection of zero indicated that demand will vanish at or before 2000, based on the historical relationship

§ **Standard for buying and selling of antimony trioxide**

1. ASTM has set the standard for commercial grades of Sb_2O_3 as follows. Sb_2O_3 content, 99.2 – 99.5 %; Impurities (As, Fe, Pb, etc), ≤ 0.5 %
2. JIS has set the standard (JIS K 8407) for commercial grades of Sb_2O_3 as the following.

Sb_2O_3	Pb	Fe	Cl	SO_4
≥ 98.0 %	≤ 0.02 %	≤ 0.01 %	≤ 0.1 %	≤ 0.01 %

3. Others. For Sb_2O_3 of other grades, the setting of standards depends on the usages, for example the standard set by Nihon Seiko Co.

3.1 Type PATOX-U: Ultra fine particle antimony trioxide. Because this is used in specialised catalyst application which requires high surface activity, the standard is set as sizes of particle at $0.01\text{--}0.02 \mu$, which gives surface area as high as $50\text{--}100 \text{ m}^2/\text{g}$.

3.2 Type PATOX-L: Course particle antimony trioxide. Because this is used in reactive applications, the standard set for the purity is the following.

Sb_2O_3	Pb	Fe	SO_4	H_2O
$\geq 99.3\%$	$\leq 0.03\%$	$\leq 0.003\%$	$\leq 0.005\%$	$\leq 0.1\%$

§ **Antimony trioxide manufacturing technology**

Antimony trioxide can be prepared from the antimony ore by using high temperature or by chemical leaching, which can be briefly described as the following.

1. By high temperature (pyrometallurgical process)

In this process we must first extract high concentration antimony metal, then pass it through the oxidation process to obtain the white residue of antimony trioxide, as shown in Figure 1. This process is rather complicated and the cost quite high.

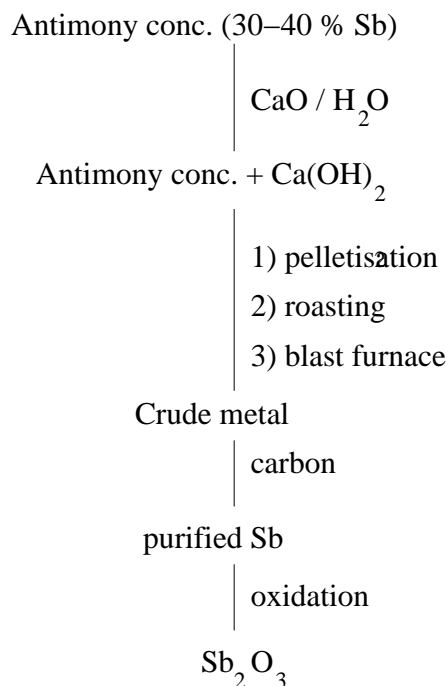


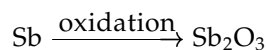
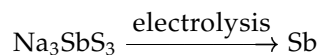
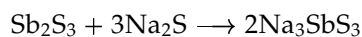
Figure 1 Flow chart showing the process of manufacturing antimony trioxide by pyrometallurgy.

2. By chemical leaching (hydrometallurgical process)

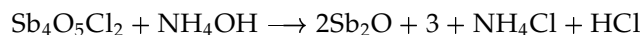
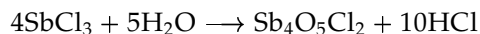
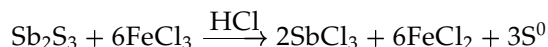
In this process we can directly prepare antimony trioxide from the ore. By using the principles of leaching and precipitation, we can easily eliminate impurities, which means a reduction in complexity and saving of energy. On top of that, we may also recycle the leaching agent.

The process of hydrometallurgy can be divided into two stages, namely

2.1 Alkali leaching. For example,



2.2 Acid leaching. For example,



Not only is the acid leaching more convenient than the alkali leaching, but we can also recycle the leaching agent (FeCl_3) for reuse by passing the solution FeCl_2 through air or oxygen gas, and the product FeCl_3 is easily obtained. Therefore this process merits a study in greater details.

The chemical extraction of ore not only is not complicated, requires lower cost and energy than extraction by heat, but can also reduce the problems of the effects on the environment that stem from the extraction by heat. Furthermore, this chemical extraction is also suitable to complex antimony ores with high impurities and difficult to extract by usual process, for example Jamesonite which is found in great quantity in the northern part of Thailand.

Because nowadays the demand of antimony trioxide in industry has greatly increased, it becomes more necessary to utilise complex- and low grade antimony ores. There is also the need to prevent the effects on the environment. Therefore chemical extraction of antimony, especially the process of acid leaching, is a technology of considerable importance both in the present and in the future.

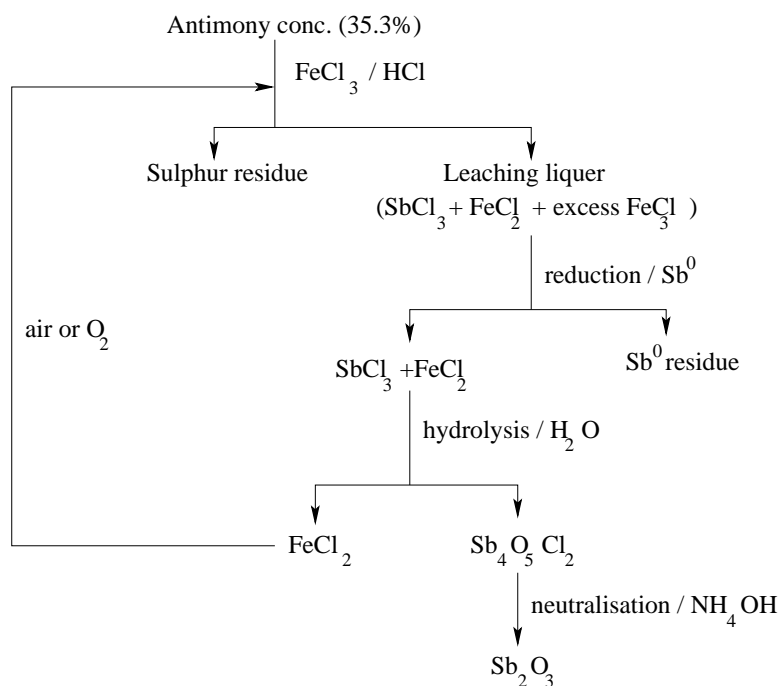


Figure 2 Flow diagram showing the process of antimony trioxide extraction.

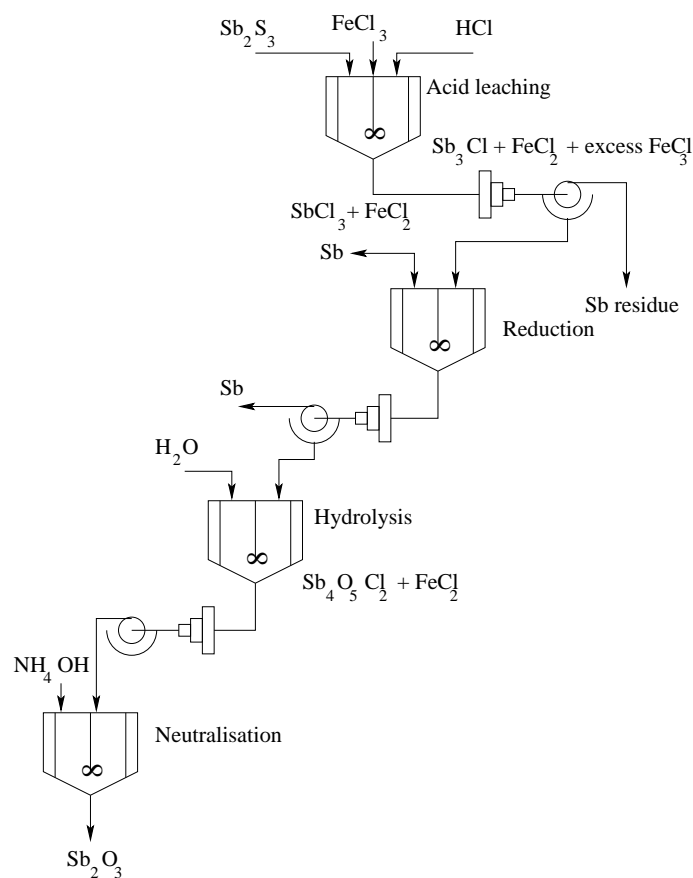


Figure 3 Flow diagram modelling the Sb_2O_3 extraction in industry.

§ 2. Experiments

§ Details of the experiments

1. Learn the methods and techniques of the processing of stibnum ore by the method of hydrometallurgy.
2. Analyse the composition of the stibnum ore sample that will be used in the analysis, in order to be able to find the suitable condition.

3. Find the suitable condition for the preparation of antimony trioxide that is in accordance with the industrial standards by studying the influence the variables have on the solubility efficiency, while maintaining high efficiency of production.

3.1 Study the effect of the temperature of solution

3.2 Study the effect of the time of solution

3.3 Study the effect of the concentration of the acid used in the solution

3.4 Study the effect of the concentration of the solution

§ **Experimental method**

1. Weigh 14.29 g of the finely crushed antimony ore (−100#).
2. Dissolve 38.93 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 7N HCl and then heat by using heating mantle until the desired temperature is reached.
3. Slowly add the weighed ore into the solution and start timing.
4. Use pipette to extract the solution at 15, 30, 45, 60 and 120 minute to assay for the amount of Sb extracted at these times.

§ **Assaying for %Sb at each condition**

1. Use pipette to extract 2ml of the extracted solution at each condition, add 100ml distilled water in order for SbCl_3 to precipitate into $\text{Sb}_4\text{O}_5\text{Cl}_2$.
2. Filter the precipitate using number 42 filtering paper.
3. Dissolve the precipitate in concentrated HCl.
4. Add 1 g tartaric acid.
5. Drop a piece of red litmus into the solution, add 50ml water.
6. Slowly turn the solution into an alkaline solution by gradually

adding NaOH until the litmus paper turns from red into blue.

7. Slowly drop concentrated HCl until the solution changes back to become acidic.
8. Add 1 g NaHCO_3 to turn the solution alkaline.
9. Add starch solution as an indicator.
10. Titrate with 0.1 N iodine solution.

§ **Method for Sb_2O_3 synthesis**

1. Dissolve 14.29 g finely crushed ore into 7N HCl in which 38.93 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ has been dissolved.
2. Filter out the insoluble parts from the solution extraction.
3. Add finely crushed Sb metal into the solution thus filtered in order to turn all the excess FeCl_3 into FeCl_2 by stirring at room temperature for approximately 2 hours.
4. Filter out the insoluble parts.
5. Dilute the solution to 0.55N HCl concentration as a hydrolysis to precipitate $\text{Sb}_4\text{O}_5\text{Cl}_2$.
6. Adjust the pH of the $\text{Sb}_4\text{O}_5\text{Cl}_2$ precipitate to 7 by using NH_4OH solution at 70°C as the neutralisation. The result is the Sb_2O_3 desired.
7. Filter and then bake dry.

§ **3. Experimental results**

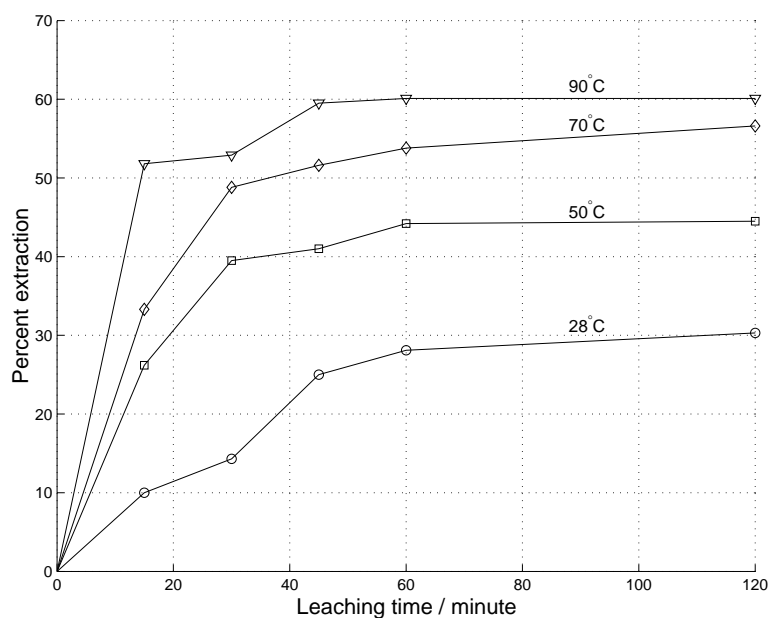
§ **3.1 Influence of the leaching temperature and time**

3.1.1 Efficiency of the extraction when leaching the ore in 7N HCl 100 ml.

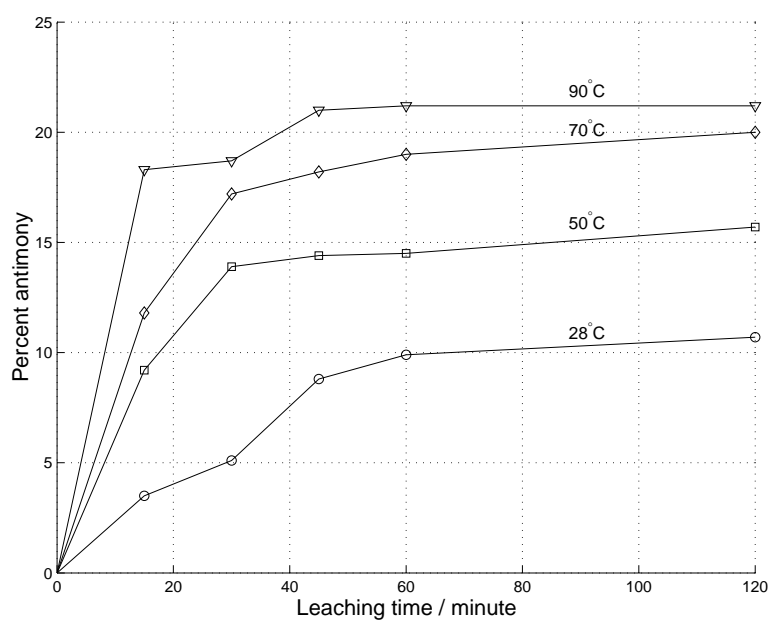
Time (minute)	Extraction temperature					
	28°C		50°C		70°C	
	% Sb	% Extr.	% Sb	% Extr.	% Sb	% Extr.
15	3.5	10.0	9.2	26.2	11.8	33.3
30	5.1	14.3	13.9	39.5	17.2	48.8
45	8.8	25.0	14.4	41.0	18.2	51.6
60	9.9	28.1	14.5	44.2	19.0	53.8
120	10.7	30.3	15.7	44.5	20.0	56.6
					21.2	60.1

Table 4 Experiment results at various time and temperature of extraction.

From Table 4 and Figure 4 we find that the efficiency and the rate of extraction increase when the extraction temperature increases from 28°C to 50, 70, and 90°C respectively. Both the efficiency and the rate of extraction become constant at temperature higher than 70°C. This means that the optimal extraction temperature must be within the range of 70–90°C.



(a)



(b)

Figure 4 Percent extraction (a), and antimony (b), when the leaching solution contains 100 ml 7N HCl and 38.93 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

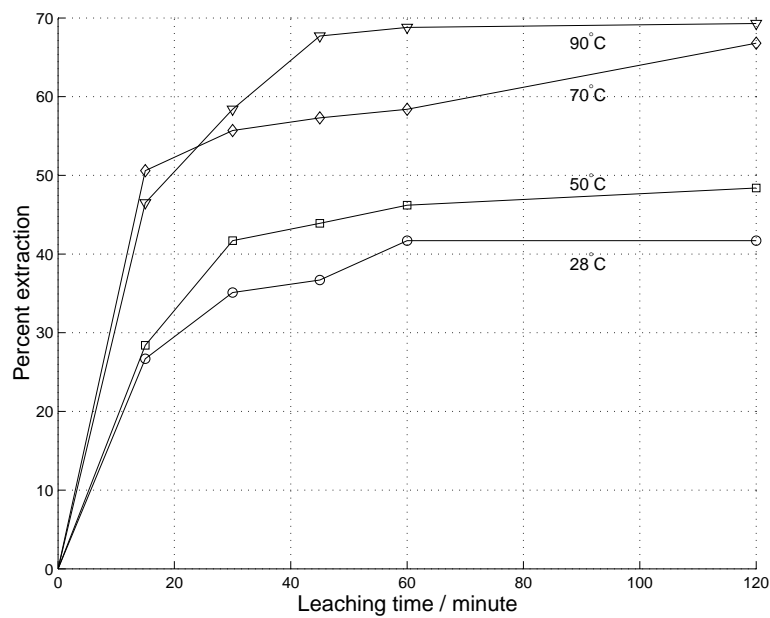
3.1.2 Efficiency of the extraction when leaching the ore in 7N HCl 300 ml.

Time (minute)	Extraction temperature							
	28°C		50°C		70°C		90°C	
	% Sb	% Extr.	% Sb	% Extr.	% Sb	% Extr.	% Sb	% Extr.
15	9.4	26.7	10.0	28.4	17.9	50.6	16.4	46.5
30	12.4	35.1	14.7	41.7	19.6	55.7	20.6	58.4
45	13.0	36.7	15.5	43.9	20.2	57.3	23.9	67.7
60	14.7	41.7	16.3	46.2	20.6	58.4	24.3	68.8
120	14.7	41.7	17.1	48.4	23.6	66.8	24.5	69.3

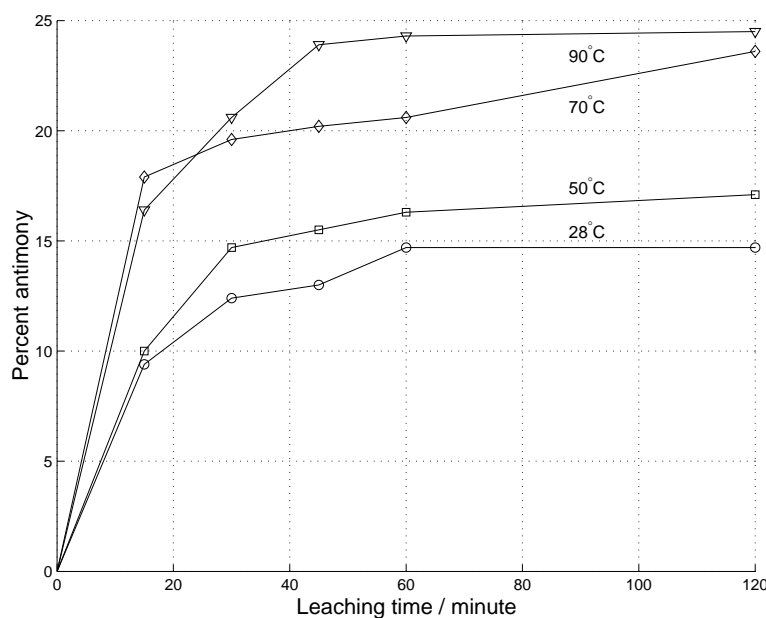
Table 5 Experiment results at various time and temperature of extraction.

From Table 5 and Figure 5 it can be seen that the efficiency and the rate of extraction increase as the extraction temperature increases from 28°C to 50, 70, [and] 90°C respectively in a manner similar to the case

where the ore is leached in 7N HCl 100 ml. But both the efficiency and the rate of extraction is higher than the previous case by approximately 10 percent. This means that the amount of acid used in the extraction by acid leaching has some influence on the efficiency and the rate of extraction.



(a)



(b)

Figure 5 Percent extraction (a), and antimony (b), when the leaching solution contains 300 ml 7N HCl and 38.93 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

§ Influence of the leach solution concentration

The controlled variables are $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 38.93 g, the concentration of HCl 7N, and the ground antimony ore 14.29 g.

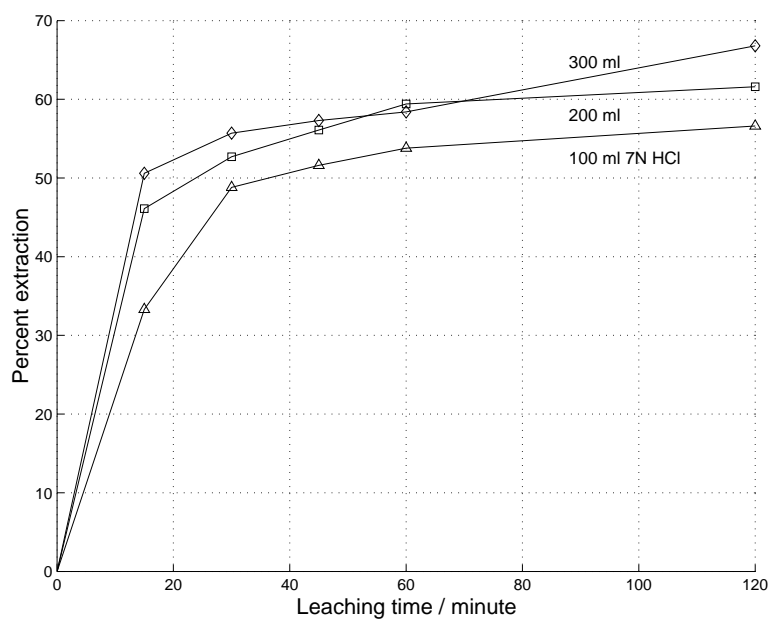
From the data in Table 4 and Table 5 we can draw Figure 6 (28°C), 7 (50°C), 8 (70°C), and 9 (90°C). [Figure 5 to 9, omitted here, compare between 7N HCl 100 and 300 ml] It can be seen that when the amount of acid used is increased from 100 to 300 ml at the extraction temperatures of either 28, 50, 70, or 90°C, the efficiency and the time of extraction invariably increase by approximately 10 percent.

When further experiments are done at the temperature of 70°C, which is a suitable temperature for the extraction in practice, the results obtained are the following. The controlled variables are 7N HCl 200 ml, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 38.93 g, and the extraction temperature 70°C.

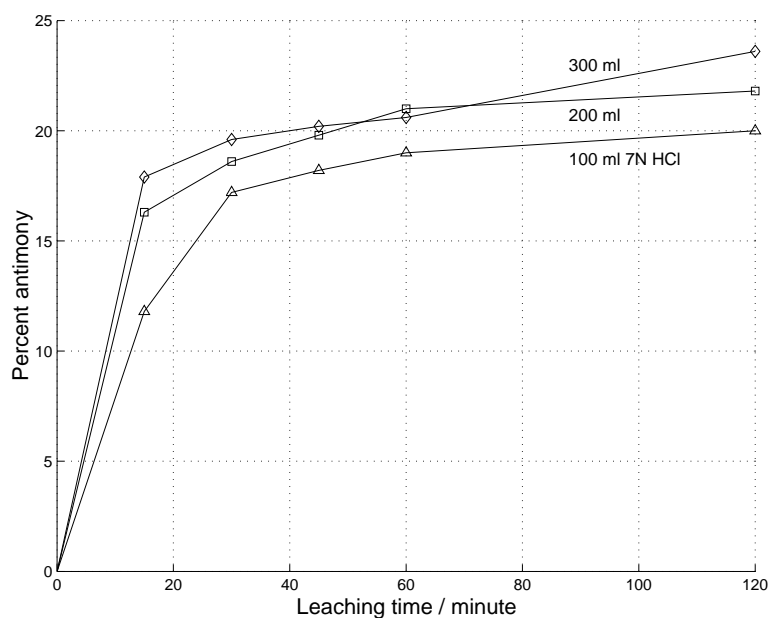
Time (minute)	15	30	45	60	120
% Sb	16.3	18.6	19.8	21.0	21.8
% Extraction	46.1	52.7	56.1	59.4	61.6

Table 6 *Experimental results at 70°C, 200 ml 7N HCl.*

From Figure 10 one finds that the efficiency and the rate of extraction at 70°C and the acid concentration 7N increase by approximately 5 percent when the acid amount increases from 100 ml to 300 ml. This means that the efficiency increases as more acid is used.



(a)



(b)

Figure 8 The effect of various amount of HCl on the extraction efficiency. Percent extraction (a), and percent of antimony (b) in the solution which contains 7N HCl 100, 200, and 300 ml, and 38.93 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, at 70°C .

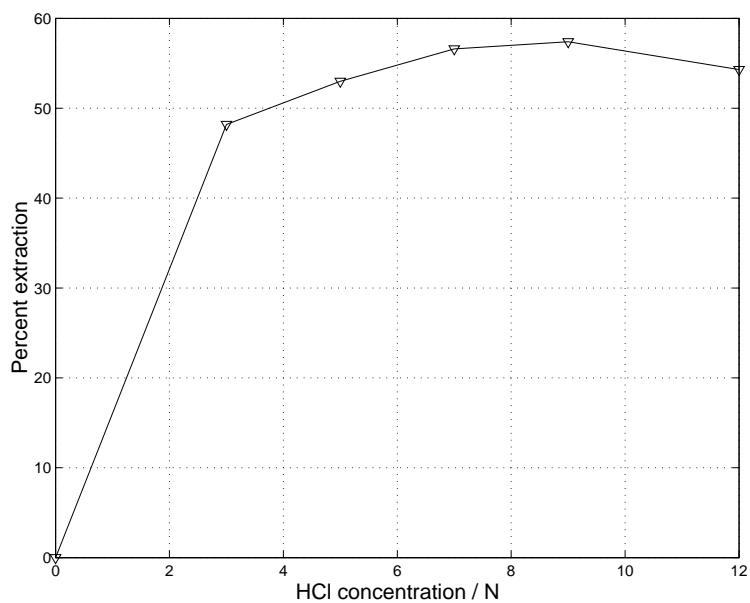
§ 3.3 Influence of the acid concentration used in leaching

The controlled variables are $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 38.93 g, HCl 100 ml, the extraction temperature 70°C , and the time of extraction 2 hours. Vary the concentration of HCl to be 3, 5, 7, 9, and 12N.

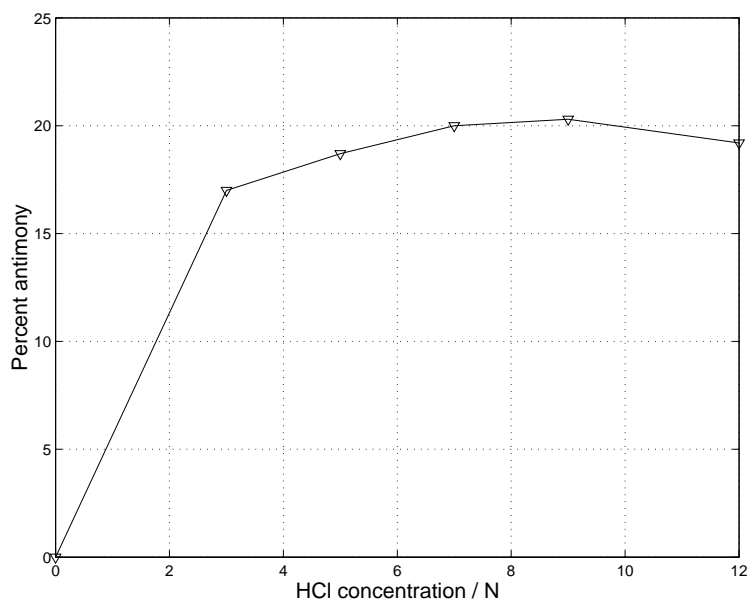
Concentration (N)	3	5	7	9	12
% Sb	17.0	18.7	20.0	20.3	19.2
% Extraction	48.2	53.0	56.6	57.4	54.3

Table 7 Experimental results at various acid concentrations.

From Table 7 and Figure 11, the efficiency of extraction is highest between the acid concentration 7 and 9N, that is the suitable concentration in practice is 7N.



(a)



(b)

Figure 11 Effect of the acid concentration on the leaching efficiency, (a) the percent extraction, and (b) the percent antimony. The leach solution contains 100 ml HCl and 38.93 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 70°C .

When precipitating Sb_2O_3 at the room temperature and at the temperature 90°C , and then take the SEM pictures of the precipitates, the results are shown in Figure 12 and 13 [omitted]. From these it can be seen that when precipitating at a low temperature, the structure of Sb_2O_3 tends to be more cubic than when precipitating at a higher temperature. Therefore if Sb_2O_3 of a cubic structure is desired, the precipitation should be done at a low temperature, while on the other hand if Sb_2O_3 of a rhombic structure is desired, it should be done at a high temperature.

§ 4. Conclusion and suggestions

From the experiments studying the influence of variables in the preparation of Antimonytrioxide from stibnum ores by hydrometallurgical method with the leaching of the ore in an acid solution of ferric chloride it was found that the production of Sb_2O_3 by hydrometallurgical process on the industrial scale has a reasonably high viability when leaching the mineral solution in the hydrochloric acid solution of ferric chloride the acidic concentration of which is between 5–9N HCl at the temperature range of $70\text{--}90^\circ\text{C}$ for approximately 1–1.5 hours and with FeCl_3 about 10–20% in excess.

§ Acknowledgements

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